

The X-ray Spectra given by Crystals of Sulphur and Quartz.

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(Received December 1, 1913,—Read January 29, 1914.)

A number of results of examination of crystals by means of the X-ray spectrometer, which have been recently obtained in this laboratory, are discussed in a paper by W. L. Bragg.* The cases which he has considered are those in which the information has been sufficient for a complete solution of the crystal structure. This note deals with two cases, viz., sulphur and quartz, which have not been completely solved, but which have nevertheless given interesting results.

In one form sulphur is orthorhombic. According to crystallographic measurements of the usual kind it has three unequal axes at right angles to each other, whose lengths are in the ratio 0·813 : 1 : 1·903. It may be assumed at once therefore that the element of structure is based on a rectangular parallelepiped of the form given in the figure. The examination of the spectra given by various planes shows that the assumption is justified.

It is convenient to say a word at this stage as to the method of preparing crystal planes for examination. Some, of course, occur as natural faces; several of the results given below were obtained from a magnificent sulphur crystal very kindly lent by Prof. Pope. Others it is necessary to cut, but the operation is a very simple one. It is not in the least necessary that the surface should be true or smooth; for the X-rays are reflected by the body of the crystal and not by the surface. It is sufficient to rub down an ordinary sulphur crystal on a piece of sand-paper, judging the result by eye. There would be no need to prepare a surface at all were it not that it is then more convenient to place the crystal correctly in its holder. Some crystals such as spinels, diamonds and rubies cannot of course be cut, and a little calculation is required

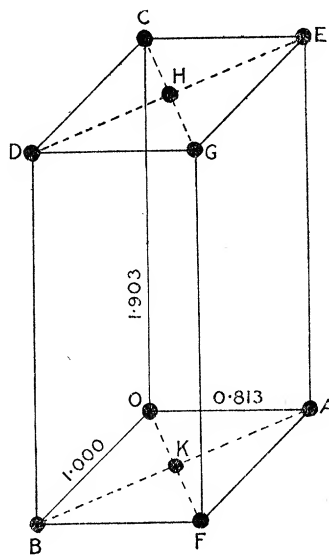


FIG. 1.

* 'Roy. Soc. Proc.,' p. 468 *supra*.

if they are to be correctly mounted; but if the mounting is difficult, and at first incorrect, the spectrometer readily gives indication as to how it is to be amended.

The X-ray bulb which was used in the examination of the sulphur had a palladium anticathode. The principal palladium line ($\lambda = 0.576 \times 10^{-8}$ cm.) was reflected by rock salt (100) at the following angles: the references are to fig. 1.

| | | | | | | | | |
|----------------|-------|------|-------|-------|------|------|-------|-------|
| Plane | | 100 | 010 | 001 | 011 | 101 | 110 | 111 |
| | | OCDB | OAEC | OAFB | AODG | BOEG | OCGF | ABC |
| Glancing angle | | 6.2° | 5.15° | 10.5° | 5.9° | 7°? | 4.07° | 4.15° |

It is at once clear that there is a connection between these figures and the crystallographic ratios 0.813:1:1.903. For example, the glancing angles for the planes (100) and (010) are 6.2 and 5.15. These are in the ratio 1:0.83; and the spacings of these planes, or rather sets of planes, are therefore in the inverse ratio, or 0.83:1. This is very close to the ratio 0.813:1. It is to be remembered that the connection between the glancing angle θ , the spacing d and the wave length λ is given by $\lambda = 2d \sin \theta$; when θ is small, the sine is of course nearly proportional to the angle itself.

Again the perpendicular from O on the plane ABC is

$$\frac{1}{\sqrt{\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)}},$$

where OA = a , OB = b , OC = c .

The value of this expression is easily found to be $b \times 0.60$. Now, the glancing angles of the planes (010) and (111) are 5.15 and 4.15, and these are in the inverse ratio of 1:1.24, which is very nearly twice the ratio just found.

In the same way the perpendiculars from the origin on the planes AFGE and BCEF are a and $1/\sqrt{(1/b^2 + 1/c^2)}$; or $b \times 0.813$ and $b \times 0.885$. These are in the ratio 1:1.09. The angles of reflection by the corresponding planes are 6.2 and 5.9. These are in the inverse ratio of 1:1.05.

Let us proceed, therefore, to examine the results of assuming the various forms of space lattice which may be associated with this figure (fig. 1). The choice is very limited, and the correct form is readily found to be that in which an atom* of sulphur is placed at each corner of the figure, and at the centres of the two faces perpendicular to the longer axis. Everything (as will presently appear) then falls into place at once, with the exception of the

* It is here assumed that there is one diffracting centre to each atom. This assumption seems to be very clearly in accord with present results.

angle of reflection by the (001) plane, an exception which is readily explained. Let us assume this form of lattice and proceed to calculate its dimensions. Two atoms are associated with each element of the lattice shown in fig. 1. Each atom at a corner is at the meeting place of eight volume elements, and one-eighth of it may be said to belong to each element. Hence the whole of these eight count as one. Each of the two atoms at the centres of faces belongs equally to two volume elements having a face in common, and half its value is to be assigned to each element. The two therefore count as one. Summing up, there are two atoms to each unit of volume.

We have now to find how many interpenetrating lattices there are.

It may be convenient at this stage to explain that the spectra given by a set of interpenetrating lattices are the same as those given by a single lattice if we consider only the positions of the first-order spectra in each case, unless it happens that the planes of one lattice exactly interleave those of the other. To make this clear, let us consider the corresponding case of the diffraction grating. A set of diffracting rulings, A, B, C, D, diffract light of a wavelength at a given angle. If an interpenetrating similar set of lines, A', B', C', D', is ruled on the same grating parallel to the first, the first-order spectrum occurs in the same place as before, though with altered intensity, unless the second set of lines happens to fall exactly half way between the first, in which case it disappears and the second spectrum becomes the first.

This principle is easily extended to the space lattice. Generally, interpenetrating similarly placed lattices give a first-order spectrum in the same place as any one of the lattices would do alone; unless they are so arranged that they can be derived from one another by movements involving equal successive translations perpendicular to any set of planes, in which case all the spectra given by that set of planes will disappear except the n th, $2n$ th, and so on.

If the translations referred to are not equal, the intensities of the spectra of the various orders given by that set of planes will not be the same, either absolutely or relatively to each other, as those given by one lattice; but the position of the first-order spectrum will be the same as if there were only one lattice.

Let us assume that there are n lattices. To every unit of volume abc there are, therefore, $2n$ atoms; for each lattice contributes two. Taking the weight of the H atom as 1.64×10^{-24} , the volume abc contains a mass

$$2n \times 32 \times 1.64 \times 10^{-24} \text{ grm.} = n \times 104.5 \times 10^{-24}.$$

The density of sulphur is 2.07, and $a = b \times 0.813$, $c = b \times 1.903$.

Hence $b^3 \times 0.813 \times 1.903 \times 2.07 = n \times 104.5 \times 10^{-24}$.

$$b^3 = n \times 32.75 \times 10^{-24}. \quad (i)$$

The glancing angle of the first-order spectrum of the (010) planes is 5.15° , and the spacing of these planes is $b/2$ for the form of lattice we have assumed.

$$\begin{aligned} \text{Thus} \quad 0.576 \times 10^{-8} &= b \times \sin 5.15^\circ \\ &= b \times 0.0898, \\ b &= 6.41 \times 10^{-8}, \\ b^3 &= 263.4 \times 10^{-24}. \end{aligned} \tag{ii}$$

Comparing (i) with (ii) it is clear that n must be equal to 8.

Substituting this value for n in (i) we have—

$$\begin{aligned} b^3 &= 262 \times 10^{-24}, \\ b &= 6.40 \times 10^{-8} \text{ cm.} \end{aligned}$$

This gives the actual dimensions of the lattice of fig. 1, and it is now easy to find the relative spacings of the various sets of reflecting planes, and therefore the glancing angles at which the first-order spectra should appear.

The next table compares the values so calculated with those actually observed.

| | | | | | | | |
|--------------------------|------|------|------|------|------|------|------|
| Plane | 100 | 010 | 001 | 011 | 101 | 110 | 111 |
| Glancing { Calculated... | 6.35 | 5.2 | 1.33 | 5.85 | 6.82 | 4.06 | 4.3 |
| angle { Observed ... | 6.2 | 5.15 | 10.5 | 5.9 | 7.0 | 4.07 | 4.15 |

Except in the case of the (001) plane, the agreement is quite satisfactory. The exception is very interesting; the angle of reflection of the first spectrum is eight times what it should be were there only one lattice. The meaning of this is clearly that the eight lattices are to be derived from each other by movements involving successive equal translations parallel to the c axis; this causes all the spectra to disappear up to the eighth, in the manner explained above.

The spectra given by sulphur are all weak, particularly in the case of the (101) plane, and in no case have any been found so far of higher order than the first. Consequently there are no available data at present for proceeding further with the calculation of the relative positions of the eight lattices.

The analysis of the quartz spectra may be carried out on much the same lines as those of the preceding argument, and a briefer discussion will be sufficient.

The results show, as would be anticipated, that it is necessary to use a hexagonal lattice, as in the figure, where $Ii = c$, $IF = a$, and $c = a \times 1.1$, according to crystallographic data.

thence the angles at which the palladium line should be reflected. These are compared with the observed values in the following table:—

| Plane..... | EDde | Ide | FDdf | Gpq | i'de | BGed | AHed | BDF |
|---------------|------|------|------|-----|------|------|-------|-----|
| Observed ... | 3·9 | 4·93 | 6·60 | 9·2 | 8·4 | 7·25 | 10·15 | ? |
| Calculated... | 3·9 | 4·95 | 6·75 | 9·1 | 8·3 | 7·3 | 9·5 | ? |

It is curious that so far no reflection has been found from the plane BDF, the plane which is perpendicular to the principal axis.

[*Note added January 6, 1914.*—Since this was written a weak reflection from this face has been found. The value of the glancing angle shows that the spacing of the planes parallel to BDF is one-third of Ii . This means that the three lattices can be derived from each other successively by movements involving equal translations parallel to the c axis. The result was to be expected.]

Many of the planes give very good reflection, and spectra of more than one order, so that it will no doubt be possible to complete the analysis of the quartz structure eventually. So far, it is clear that there are three interpenetrating lattices of the given form for every atom in the molecule. The three must no doubt be arranged as suggested by Groth, so that they can be derived from each other successively by a translation equal to $c/3$ along the c axis accompanied by a rotation of 120° about a line parallel to that axis. This constitutes a screw motion, which may be either right- or left-handed. It remains to complete the determination of the positions of the silicon and the oxygen lattices with reference to the line of rotation.
